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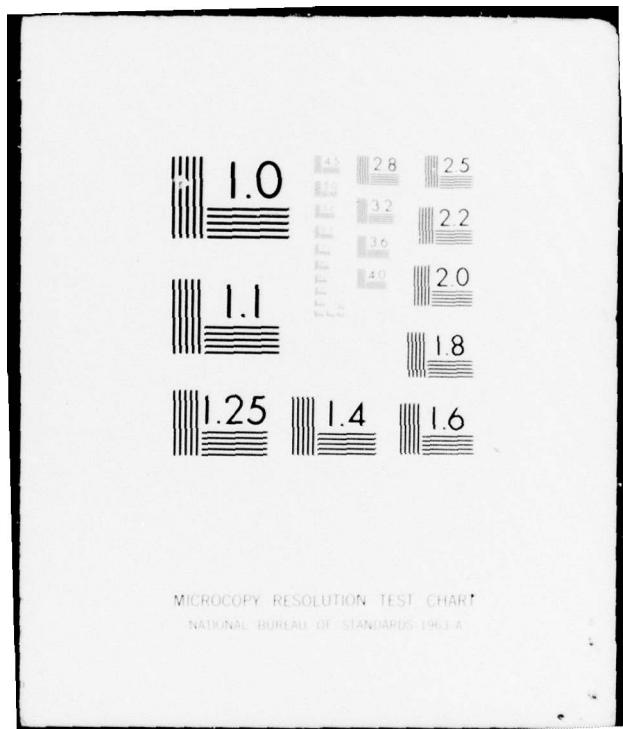
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X_a CALCULATION OF TRANSITION ENERGIES
IN MULTIPLY IONIZED ATOMS

D. A. Ringers

July 1977

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Electronic Excitations, X-Alpha Method and Transition Energies		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (hmn) The X _α method has been applied to the calculation of ionization energies in multiply ionized atoms. It is shown that the accuracy of calculations can be improved if appropriate (different) values of α are used for each configuration. Alternatively, one can use the Slater transition state, wherein a total energy difference is related to a difference in single-electron eigenvalues. By a series expansion, the value of α for an excited configuration can be related to its value for the ground-state configuration. The terms $\Delta\alpha(\partial E/\partial\alpha)$,		

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thus introduced, exhibit a similar dependence on atomic number as the ground-state values of α . Results of sample calculations are reported and compared with experiment.

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I. INTRODUCTION

An increasing need has recently arisen for comprehensive theoretical work on transition energies, x-ray emission rates and Auger transition probabilities pertaining to multiply ionized atoms. Theoretical information on these atomic quantities is required to interpret a growing body of data derived from ion-atom collision experiments, beam-foil spectroscopy, data expected to arise from astrophysical processes¹, and data from experimental programs in combustion and erosion.

II. THEORY

In order to compute transition energies we have used the $X\alpha$ method². The $X\alpha$ eigenvalues and eigenfunctions agree closely with results from the Hartree-Fock (HF) method for closed-shell atoms and from the Hyper-Hartree-Fock (HHF) method for open-shell atoms³. And, with its local approximation to the exchange, the $X\alpha$ method leads to computational simplifications. The concept of the transition state⁴, whereby the ionization energy, a difference in total energy is well approximated by a single-electron eigenvalue, can be readily implemented in the $X\alpha$ theory. The transition-state concept avoids the necessity of carrying out two high-precision calculations, one for the initial-state total energy and one for the final-state total energy, which is usually necessary in the HF or HHF frameworks. Instead, it is possible to calculate directly a total energy difference. The $X\alpha$ method can also be extended to molecules and solids, whereas the HF method is in practice only useful for isolated atoms. It can be shown that Fermi statistics and the Hellman-Feynmann and virial theorems are inherently satisfied^{5,6}. The transition-state concept is finding increasing application and has been providing results in good agreement with experiment. So far, however, the method has not been utilized to achieve the accuracy of which it is capable. Thus, deviations of 10 eV from experimental binding energies of ~ 200 eV have been noted⁷. Considerable improvement is possible, as indicated below.

1. T. Bunch, L. Caroff, and Hans Mark, in Atomic Inner-Shell Processes, edited by B. Crasemann (Academic Press, New York, 1975).
2. Slater, J.C., Advances in Quantum Chemistry, edited by P.O. Lowdin, (Academic Press, New York, 1972).
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7. Beebe, N.H.F., Chem. Phys. Lett. 19, 290 (1973).

Generally, in an atomic (or molecular, or solid) Slater transition-state calculation, a value of α for the neutral-atom ground-state configuration is used⁸. This procedure does not achieve the potential inherent in the method, particularly for inner shells. The problem lies in the fact that the value of α which is appropriate for the ground state is not appropriate for an ion with one or more inner-shell vacancies. In the $X\alpha$ theory, the total energy is a functional of α , and since the virial theorem expresses a relationship between the kinetic and potential energy of the system, one might expect different values of α to satisfy the virial theorem for the ground and excited states. To calculate the difference between the ground total energy $E_0(\alpha_0)$ and an excited-state total energy $E_e(\alpha_e)$, it is therefore necessary to relate the excited-state α_e to the ground-state α_0 .

The original Slater transition-state concept for the process of ionization may be derived from an expansion of the total energy⁹ and can be expressed by the relation

$$E_0(\alpha_0) - E_e(\alpha_0) = \frac{\partial E}{\partial n_i} \Big|_r = \varepsilon_i, \quad (1)$$

where ε_i is a single-electron eigenvalue of a state with occupation number halfway between the initial-state and final-state occupation numbers, and n_i is this occupation number, which formally need not be integral, evaluated at the reference state indicated by the subscript r . We expand

$$E_e(\alpha_e) = E_e(\alpha_0) + \Delta\alpha \frac{\partial E}{\partial \alpha}, \quad (2)$$

where $\Delta\alpha$ stands for the difference $\alpha_e - \alpha_0$. Taking account of the change in α , we therefore have

$$E_0(\alpha_0) - E_e(\alpha_e) = \varepsilon_i - \Delta\alpha \frac{\partial E}{\partial \alpha}. \quad (3)$$

It has been common to use $E_e(\alpha_0)$ instead of $E_e(\alpha_e)$, neglecting the term $\Delta\alpha(\partial E/\partial \alpha)$; this is reasonable for outer shells. However, for inner shells it is often necessary to retain the additional term. In particular, this term cannot be neglected in calculations of Auger and Coster-Kronig

8. Schwarz, K., Phys. Rev. B 5, 2466 (1972).

9. Slater, J.C., and J.H. Wood, Int. J. Quant. Chem. tr, 3 (1970).

transitions, in which the energy of the emitted electron can be of the order of only a few eV. If neither the initial nor the final state is the ground state, two terms of the form $\Delta\alpha(\partial E/\partial\alpha)$ appear on the right hand side of Eq. (3).

III. RESULTS AND DISCUSSION

We have determined these additional terms and computed certain transition energies for a few multiply ionized atoms in order to test the approach. Preliminary calculations indicate that $(\partial E/\partial\alpha)$, while differing for each shell of a given atom, can be reasonably well approximated for most shells by the corresponding value calculated by Schwarz⁸ for neutral atoms. The factor $\Delta\alpha$ seems, from our preliminary calculations, to be a nearly linear function of Z for a given shell, behaving in much the same way as the ground-state α 's⁸ (Figs. 1-3).

Selected nonrelativistic values of $\Delta\alpha(\partial E/\partial\alpha)$ are listed in Table I. With these terms, relativistic binding energies were derived that agree quite well with measurements¹⁰ (Table II). As a further test of the method, we have calculated the energies of a few selected x-ray satellites and tentatively identified them with measured non-diagram, or satellite lines (Table III). A satellite line occurs near a relatively low lying energy level as a result of a rearrangement of the outer electrons.

Recent work¹¹ has indicated that the energy difference between the $K\beta'''$ satellite in aluminum, which has been attributed to a $KL_{2,3} \rightarrow L_{2,3}M$ transition¹², and the $K\alpha$ satellite, which is due to a $KL_{2,3} \rightarrow (L_{2,3})^2$ transition¹³, should be equal to the energy of the $L_{2,3}$ satellite $(L_{2,3})^2 \rightarrow L_{2,3}M$ and have a value of 15.2 ± 0.3 eV. Calculation of these transition energies by the $X\alpha$ method yields a value of 13.8 eV, which is in good agreement with the experimentally obtained value.

10. Siegbahn, K., C. Nordling, G. Johnsson, J. Hedman, P.F. Heden, K. Hamrin, V. Gelius, T. Bergmark, L.W. Werme, R. Manne and Y. Baer, ESCA: Applied to Free Molecules, (North-Holland, Amsterdam, 1969).
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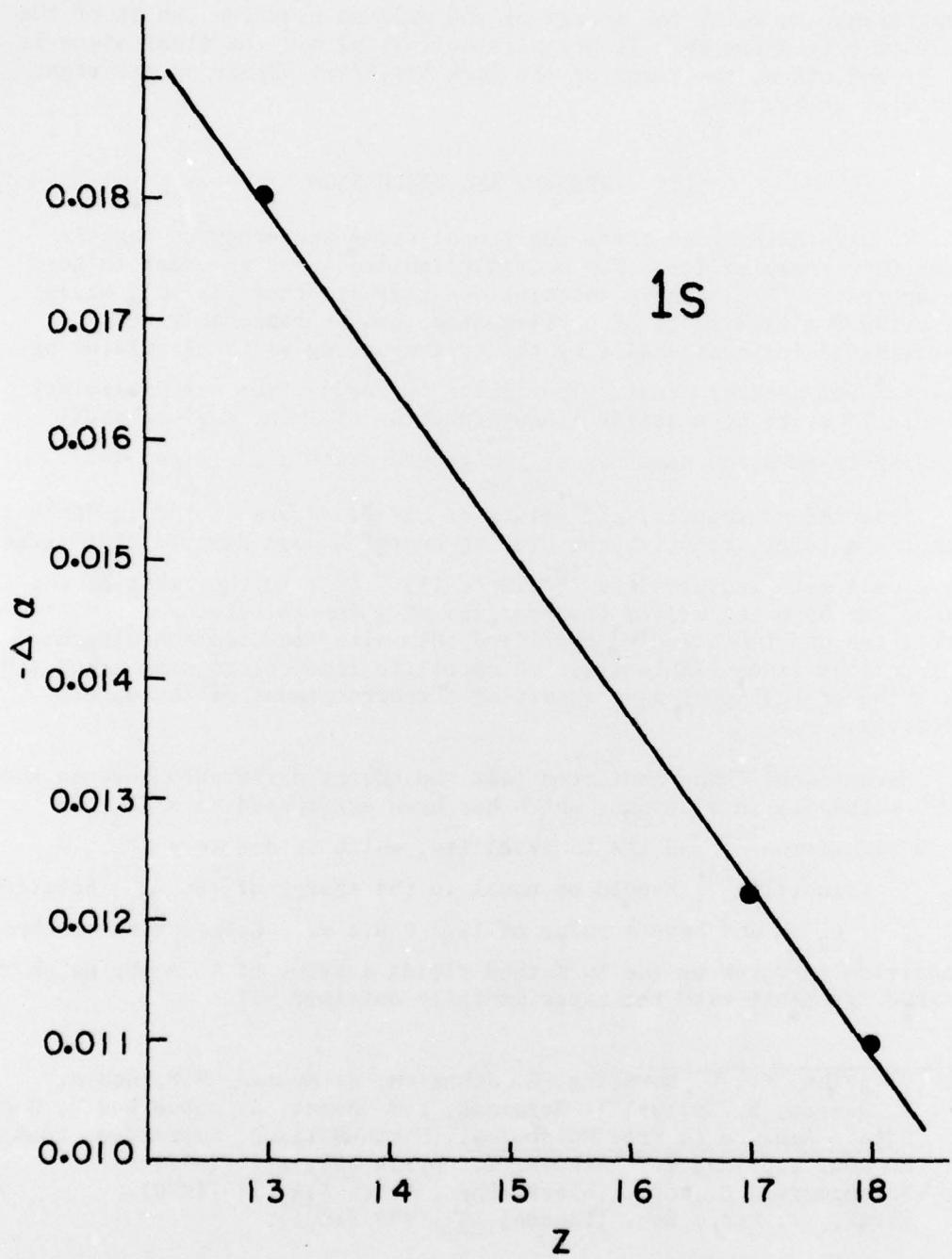


Figure 1. The term $\Delta\alpha$, as a function of Z , for the 1s shell of selected atoms for which the outermost electrons are in the 3p state.

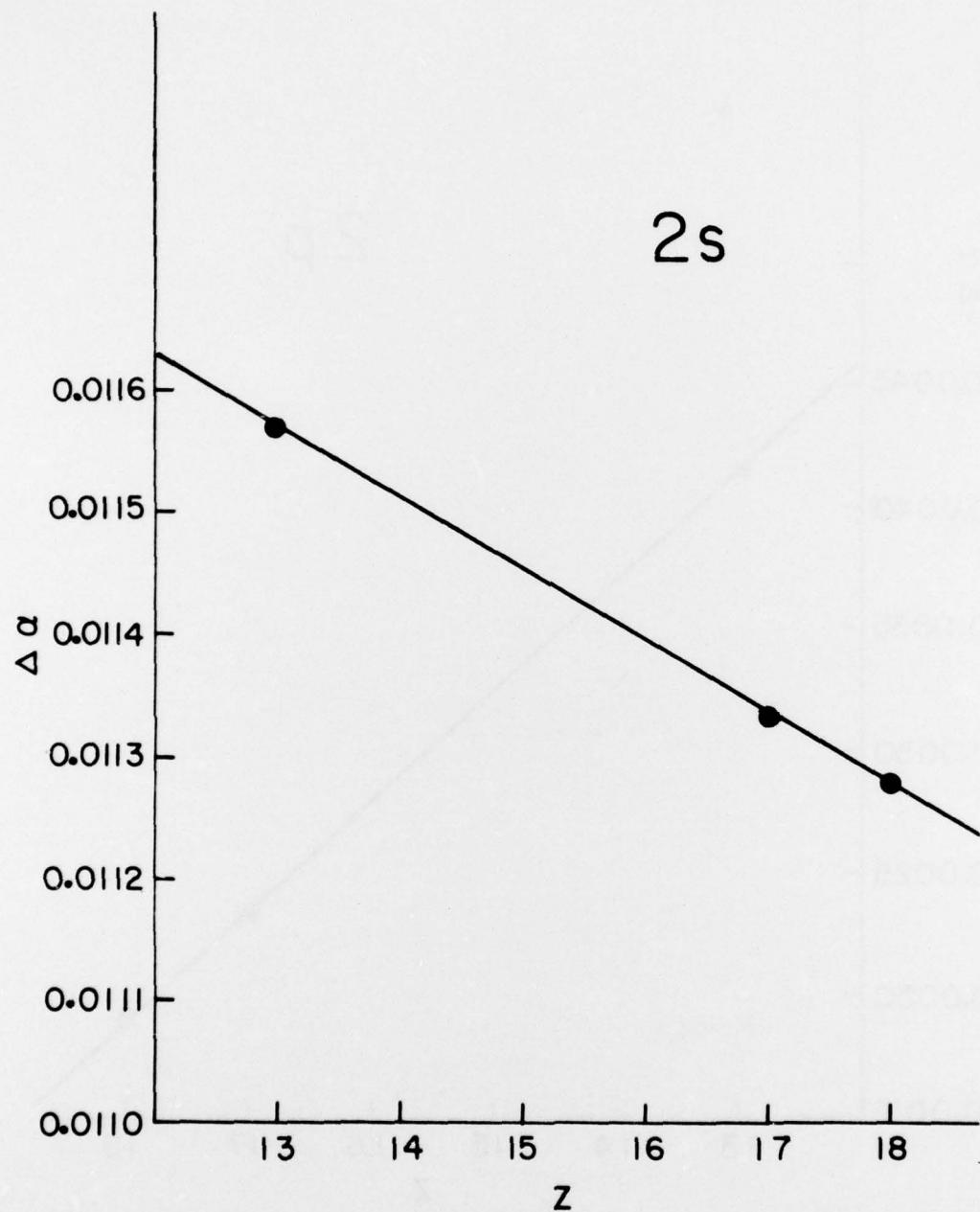


Figure 2. The term $\Delta\alpha$, as a function of Z , for the 2s shell of selected atoms for which the outermost electrons are in the 3p state.

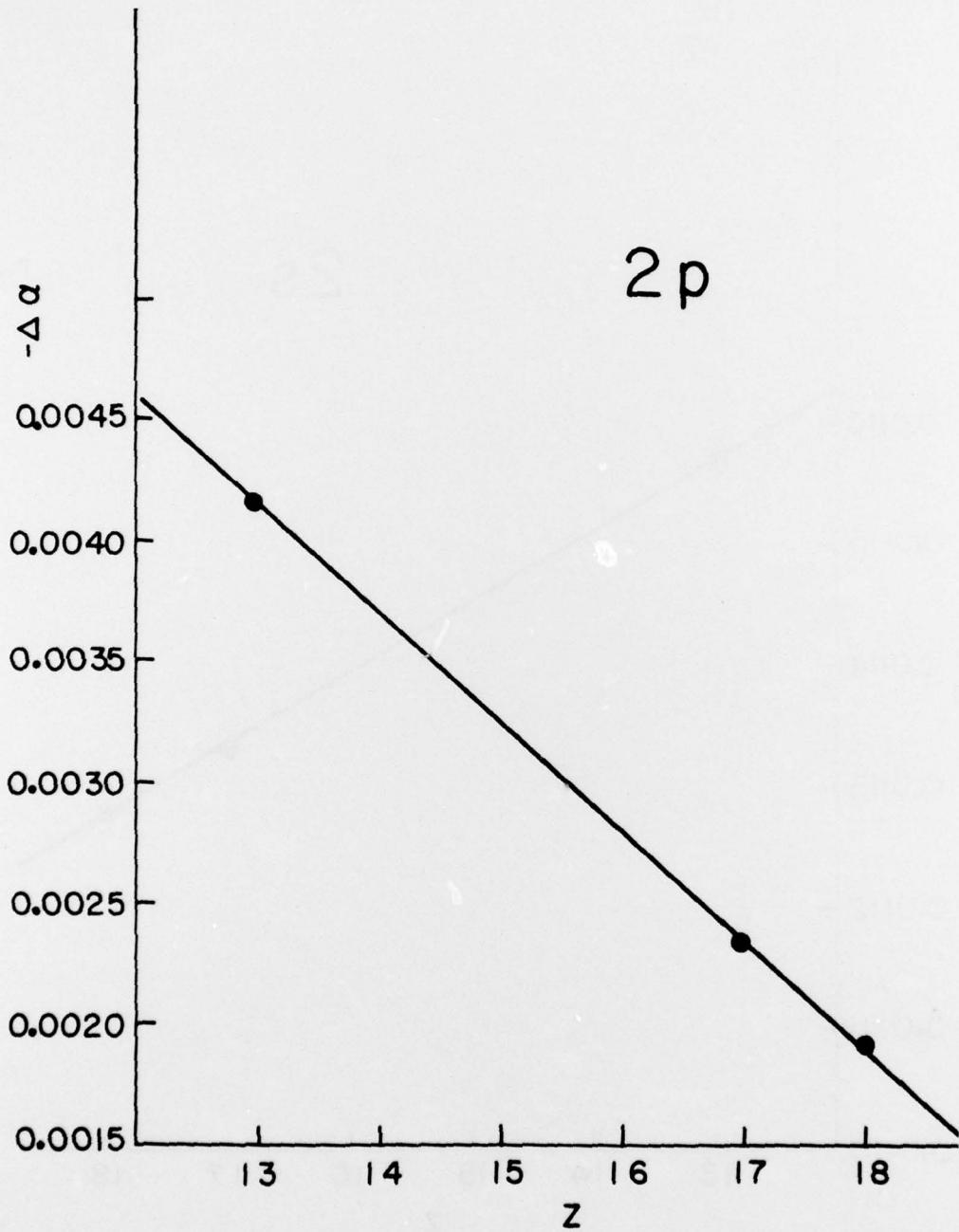


Figure 3. The term $\Delta\alpha$, as a function of Z, for the 2p shell of selected atoms for which the outermost electrons are in the 3p state.

Table I. Values of $\Delta\alpha(\partial E/\partial\alpha)$ for Selected Transitions.

Removed Electron	$\Delta\alpha(\partial E/\partial\alpha)$ (eV)		
	Al	Cl	Ar
1s	-9.81	-10.46	-10.41
2s	7.38	11.15	12.28
2p	-2.66	- 2.29	- 2.02
3s	-0.93	1.97	3.40
3p	0.23	- 0.74	- 0.81

Table II. Relativistic Binding Energies in Neutral Ar (in eV).

Electron	$\epsilon_i(\alpha_0)$	$\epsilon_i(\alpha_0) - \Delta\alpha \frac{\partial E}{\partial\alpha}$	Experiment ^a
1s	-3220.6	-3210.2	-3206.0
2s	- 314.8	- 327.0	- 326.3
$2p_{1/2}$	- 252.1	- 250.1	- 250.6
$2p_{3/2}$	- 250.1	- 248.1	- 248.5

^a Measured binding energies, from Ref. 10.

Table III. Experimentally Observed X-Ray Satellite Lines and Theoretically Derived Transition Energies in Multiply Ionized Atoms.

Element	Diagram Line	Satellite Line	Energy Difference (eV)	Ref.	Experiment		Theory ^a	
					Initial Vacancy Configuration of Satellite	Final Vacancy Configuration of Satellite	Energy Shift With Respect to Diagram Lines (eV)	
Al	K α_2	K α'	5.69	15	1s2p	3P 2p, 2p	6.90	
	K α_2	K α_4	11.85	15	1s2p	1D 2p, 2p	12.00	
	K α_2	K α_5	19.71	15	1s2p	1S 2p, 2p	19.63	
	K α_2	K α_6	23.56	15	1s2p	2p, 3s	23.15	
	K α_2	K α'	10.73	15	1s2p	3P 2p, 2p	10.92	
	K α_2	K α_3	17.44	15	1s2p	1P 2p, 2p	18.24	
Cl	K β_1^V	K β^V	2.44	15	1s3p	3P 3p, 3p	2.36	
	K β_1^V	K $\beta'1$	8 ^b	16	1s3p	1S 3p, 3p	7.20	
	K β_1^V	K β_3^V	3.3	16	1s3p	1D 3p, 3p	3.80	

^a Present work.

^b Scaled from graph in Ref. 14.

14. Druyvesteyn, M.J., Z. Physik 43, 707 (1927).
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16. Larkins, F.P., J. Phys. B4, 1 (1971).

IV. CONCLUSIONS

A consideration of the appropriate value of the exchange-correlation parameter for each configuration leads to improved results for ionization energies in multiply ionized atoms, when calculated by the formalism of the $X-\alpha$ theory. The terms $\Delta\alpha$ vary with atomic number in a manner similar to the variation of the ground state α values.

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